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**PEMOCVD Ferroelectric Nonvolatile Radiation-Hard Memories:  
Phase I Final Report**

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**INTRODUCTION**

The purpose of this Phase I effort was to determine the feasibility of depositing ferroelectric lead zirconium titanium oxide (PZT) thin films using plasma enhanced-metalorganic chemical vapor deposition (PEMOCVD). To obtain PZT films that are useful for integrated circuit ferroelectric memories, the films should be deposited directly in the perovskite phase at the lowest possible substrate temperatures. This would circumvent problems from high temperature deposition and annealing that have hindered development of ferroelectric thin film devices. These problems include thermally induced strain in the films and incompatibility with standard semiconductor processing. Useful PZT films also must have high purity, uniform stoichiometry, and should be deposited conformally. The PEMOCVD process was chosen for this effort because it appears to have promise for reaching these film quality goals. Results so far indicate that perovskite PZT films can be grown below 400 °C by PEMOCVD.

Low temperature deposition is critical to ferroelectric thin film processing because it may reduce aging and fatigue found in these films (1). Deposition or annealing at temperatures high enough to produce significant thermal expansion mismatch between substrate and film can create large internal strains in the final film. Over time, reorientation and clamping of ferroelectric domains may occur to relieve strain at domain walls and grain boundaries. This is thought to be a primary mechanism for aging, and possibly fatigue with microcracking. Therefore, lower deposition temperatures for crystalline or polycrystalline ferroelectric PZT films is a key goal in this effort. This will allow direct investigation of this theoretical aging and fatigue mechanism.

In addition to improving basic film properties, there are important commercial reasons to pursue low temperature perovskite deposition. First, it should create a wider choice of materials for electrodes. Problems arising from inter-diffusion of metals between ferroelectric, electrodes, and underlying substrates have impeded device fabrication attempts. Keeping temperatures low may allow use of electrode metals that are highly soluble in PZT at annealing temperatures. Second, it should dramatically lower the development cost for integrated semiconductor devices that incorporate ferroelectric thin films. This is because the ferroelectric film could be deposited on top of complete silicon or gallium arsenide devices that contain standard aluminum metallization which would melt below ferroelectric annealing temperatures. Presently annealing of the ferroelectric must precede metallization - meaning that the ferroelectric constituent metals must be introduced at a midpoint in the integrated device fabrication process. Therefore a virtually complete new semiconductor process line must be dedicated to ferroelectric device development, in order to avoid contaminating an existing process line. Low temperature perovskite film processing would save the cost of a dedicated process line by placing the ferroelectric deposition at the final device fabrication steps, thus isolating the metals from the semiconductor process.

Impurities in the storage capacitor dielectric film material are a critical factor in semiconductor memory performance, since they can act as dopants contributing to leakage current, loss tangent, and dielectric breakdown. In this effort, impurity reduction is addressed by two means. First, maintaining low deposition temperature reduces volatilization of potential contaminants from the

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deposition chamber walls and fixtures. Second, the metalorganic starting materials in gas or liquid form can be purified to a high degree and conveniently checked for contaminants. Perhaps the most significant impurity source in metalorganic CVD is incorporation in the film of residual carbon from the precursors themselves. This must be eliminated by ensuring that film formation by-products are completely volatile and exhausted from the chamber. Maintaining oxygen partial pressure sufficient to oxidize all carbon by-products is one possible way to accomplish this. Another way is to modify the chemical structure of the metalorganic precursors.

MOCVD can achieve tight control of film composition, as demonstrated by its use to fabricate GaAs/AlGaAs and HgTe/CdTe superlattices (2,3). For ferroelectric materials, composition uniformity at microscopic scale is necessary to obtain films with high phase purity. Using MOCVD, composition uniformity is attained by thorough mixing of film precursors in the gas phase. If precursors of each constituent metal have suitable volatility, stoichiometry can also be well controlled by regulating precursor temperature and carrier flow rates. Also, if competitive side reactions occur to form mixed oxide phases in the film, these may be reduced by adjusting reactor conditions and precursor chemical structure. This situation contrasts with that for sputtered metal oxide films, where different sputter rates for constituent metals can make stoichiometry changes from target to film difficult to characterize and control (4).

Since CVD films are grown by reactions occurring under near equilibrium conditions at the growth surface, the films conformally coat surface features. This becomes a critical reliability factor for integrated memory devices in which electric field concentrations in the dielectric due to thickness variations must be avoided. This assumes particular importance when ferroelectric films are considered for high density memories. As is well known, sputter and sol gel techniques do not provide conformal films with uniform thickness.

In light of these attributes of MOCVD, and of previous experiments outlined below, MOCVD combined with *remote* plasma enhancement merits attention as a means to achieve practical ferroelectric thin film devices. The ultimate goal of this program is to deposit crystalline films below 400 °C, with high purity and uniformity. The fabrication process must be commercialized for producing reliable nonvolatile ferroelectric memories. In Phase I, films were deposited in a test PEMOCVD set-up. The results show that ferroelectric behavior can be found in films grown at 350 °C. Although preliminary, these results do justify more development of PEMOCVD as a potential method for commercial ferroelectric thin film production.

## BACKGROUND

Several recent experiments have deposited PbTiO<sub>3</sub> and PZT films using MOCVD. Metalorganic compounds were chosen as precursors because many metal alkyls, alkoxides, and aryls, for example, have high vapor pressures and pyrolyze at moderate temperatures. This makes them attractive precursor candidates for CVD of films at low temperatures on a wide variety of substrates. Two groups have obtained highly oriented crystalline PbTiO<sub>3</sub> films, with the *c* axis lying in the substrate plane, using tetraethyl lead and titanium *iso*-propoxide as MOCVD precursors. Kwak, et. al., presented x-ray diffraction patterns indicating nearly pure perovskite phase in films deposited on fused quartz at 500°C (5). Swartz, et. al., using a substrate temperature of 450°C, also found nearly pure perovskite in PbTiO<sub>3</sub> films deposited on fused silica, and no evidence of non-perovskite phase in films deposited on Pt-coated alumina (6). More recently Okada, et. al., have reported growing perovskite PbTiO<sub>3</sub> and PZT films, with the *c* axis normal to the substrate, on MgO(100) at 600°C. Their precursors were tetraethyl lead, titanium *iso*-propoxide, and zirconium tetrakis(isopropoxy)methane (7). The deposition temperatures in these experiments are at or near the post-deposition annealing temperatures commonly used for sol-gel lanthanum doped PZT (PLZT) films. Therefore, none of these results required post-deposition annealing.

These results using thermally activated MOCVD are highly encouraging. They clearly show that readily available metalorganic compounds can be oxidized to directly produce perovskite PZT films. The question remains whether an alternative to substrate heating can be found to activate the oxide forming reactions. Plasma enhancement realized by use of a flowing afterglow reactor is the approach taken here. The flowing afterglow reactor was long used for studies of gas phase reaction kinetics until it was superseded by methods such as laser induced fluorescence and flash photolysis (8). These reactors have been well characterized and used to accumulate a large body of data on homogeneous gas phase reactions; several good reviews on their design and use are available (9). They have more recently been applied in the semiconductor industry to low damage photoresist stripping and dry etching of silicon, nitride, and compound semiconductors (8). In adapting the flowing afterglow reactor to thin film growth, the technique is often referred to as remote plasma CVD (RPCVD).

RPCVD has been used to deposit a variety of thin film materials with good results. Meiners (10) grew SiO<sub>2</sub> for MOS capacitors on silicon by reacting SiH<sub>4</sub> with remotely activated O<sub>2</sub> at 300°C. A midgap surface state density of  $2 \times 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$  was found, this was an order of magnitude reduction over films previously grown by conventional plasma enhanced CVD at comparable temperatures. Richard, et.al. (11) reported elimination of Si-H bonds and near elimination of -OH groups, as detected by IR spectroscopy, in SiO<sub>2</sub> films grown from SiH<sub>4</sub> and O<sub>2</sub> in the presence of remotely activated NH<sub>3</sub> or N<sub>2</sub>. Helix, et. al. (12) showed elimination of oxygen contamination to better than 1 at.% in stoichiometric Si<sub>3</sub>N<sub>4</sub> films grown at 300°C, using remotely activated N<sub>2</sub> both for reaction with dilute SiH<sub>4</sub> and also for pre-deposition scavenging of water and oxygen from their chamber. Toyoshima, et. al. (13) used remotely generated Ar (<sup>3</sup>P<sub>2</sub>) to activate SiH<sub>4</sub>, producing a gas stream in which they could detect only emission at the SiH ( $A^2 \Delta - X^2 \pi$ ) transition wavelength. This was used to deposit amorphous hydrogenated silicon (a-Si:H) films at 400°C with predominately monohydride bonding. Rudder, et. al. (14) reported epitaxial growth of Ge and Si using metastable excited He to activate GeH<sub>4</sub> or SiH<sub>4</sub> on Ge, Si, or GaAs substrates below 300°C. They also used *in-situ* pre-sputtering with an H<sub>2</sub> plasma to promote epitaxial film growth. Huelsman and Reif (15) claimed increasing GaAs growth rates by two orders of magnitude at substrate temperatures below 600°C by using a remote plasma to crack AsH<sub>3</sub> for reaction with trimethylgallium (TMG). In this and previously reported schemes for GaAs growth by RPCVD, the TMG and substrate are isolated from the AsH<sub>3</sub> plasma.

The key distinguishing feature of plasma enhancement in a flowing afterglow reactor is the physical separation of the plasma discharge from the substrate. This leads to several advantages which all the diverse efforts in stripping, etching, and film growth cited above have sought to exploit. One advantage is the avoidance of film and substrate damage arising from high energy electron and ion bombardment of a workpiece placed within a plasma, as in parallel plate reactors. Another is that the chemical environment created at the workpiece can be more easily controlled than in conventional plasma enhancement. Etching or film growth reactions can be made to proceed along well defined paths involving few intermediates and products. This contrasts with conventional plasma enhanced CVD in which multiple branching reactions involving energetic radicals and ions must be fine tuned, if indeed the reactions can be fully delineated. Finally, the flowing afterglow reactor avoids exposing precursors directly to the plasma. This exposure can lead to nucleation of particles in the gas phase away from the substrate. These particles can contaminate the film or accumulate on the reactor walls to create a new source of volatile contaminants.

## EXPERIMENTS

### Methods

#### Reactor and Deposition System

The film deposition reactor used here is a remote plasma enhanced chemical vapor deposition configuration shown in Figure 1. This set-up is simply a gas flow tube in which a plasma glow discharge is maintained upstream from precursor injection inlets and a heated substrate block. As shown, there are three zones: the plasma discharge, the flowing afterglow, and the film growth/processing area. Film growth reactions are activated by the flow of excited state atoms and molecules from the plasma discharge to the film processing zone, instead of relying solely on thermal activation by the heated substrate. As noted above, this reactor design isolates the glow discharge from the film growth region by restricting the discharge to the region near the gas flow inlet. This protects the substrate and film from UV radiation and high energy electron and ion bombardment damage. It also avoids precursor dissociation to energetic ions and radicals that can undergo gas phase reactions leading to particle nucleation or reactor wall condensates that can generate film contaminants.

In operation, neutral and charged products from the discharge flow into the main reactor tube, constituting the afterglow. Film deposition precursors and possibly secondary activating species are injected downstream through a perforated ring or showerhead. Reactants can be injected at various points along the flow corresponding to specific relaxation times for afterglow species. Finally the temperature-controlled substrate holder is also placed in the afterglow-mixed precursor stream. The substrate and holder can be electrically floated or biased independently of the plasma parameters. The overall reactor pressure and gas flow rate are determined by the carrier and buffer gas flow. The other controllable parameters are afterglow excited state energies and concentrations, film precursor concentrations, precursor injector position, substrate temperature, and substrate bias.

In the test PEMOCVD set-up used for these studies, the reactor was a quartz tube with 8 cm inner diameter. As shown in Figure 1, the plasma electrodes were concentric steel tubes in a feed-through centered in the reactor baseplate. The 2 cm diameter outer electrode was electrically grounded with the baseplate. The 13.56 MHz plasma excitation voltage was applied to the 1 cm diameter inner electrode. The inner electrode extended 1.5 cm above the outer electrode. The plasma feed gas was brought in to the space between the electrodes. A 6 mm diameter pyrex tube centered in the inner electrode and extending 1.5 cm beyond this electrode was used to inject the metalorganic precursor mixture. The glow discharge was mainly confined to the area between the electrodes and extending nearly to the opening of the injector tube, as indicated by shading in Figure 1. Under some conditions a faint discharge glow filled the reactor volume from the base to the substrate surface. Care was taken to ensure that plasma discharge did not occur inside the pyrex injector tube. This could occur at excessive RF power levels. In most deposition trials, the RF power was held at 100 W.

The overall PEMOCVD test system used here is shown in Figure 2. Helium was used as both metalorganic carrier, buffer, and plasma feed gas. Total helium flow was regulated by mass flow controllers, with a pressure of approximately 1 atm maintained at all the controller inlets. As shown, the precursors for all three constituent metals were mixed in a manifold external to the reactor. A dilution line was included to help prevent precursor condensation in the manifold. The system vacuum was generated by a mechanical pump with approximately 60 cfm speed. Reactor pressure was regulated primarily by control of helium flow to the buffer gas feed line.

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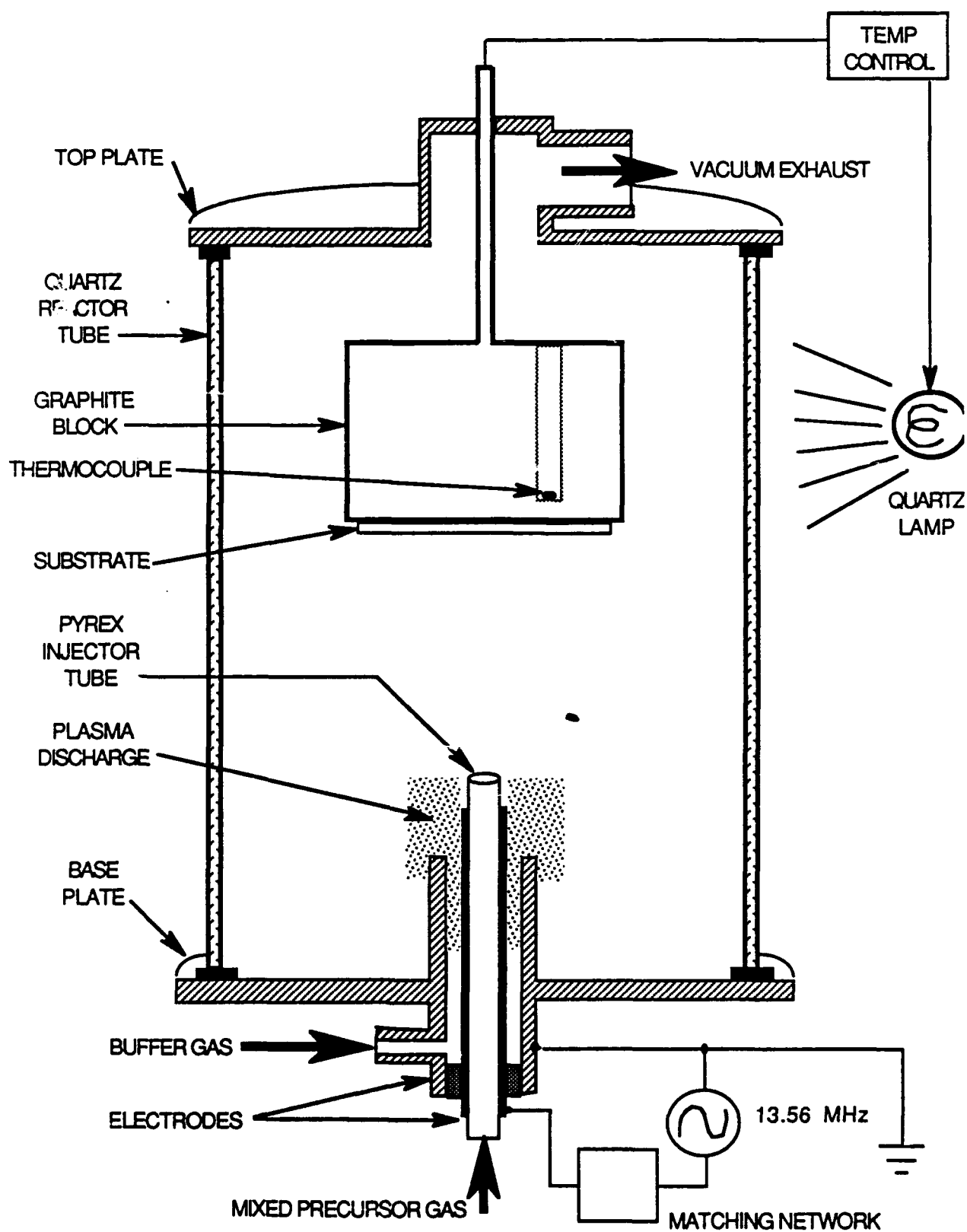


Figure 1. Deposition reactor chamber in test PEMOCVD set-up.

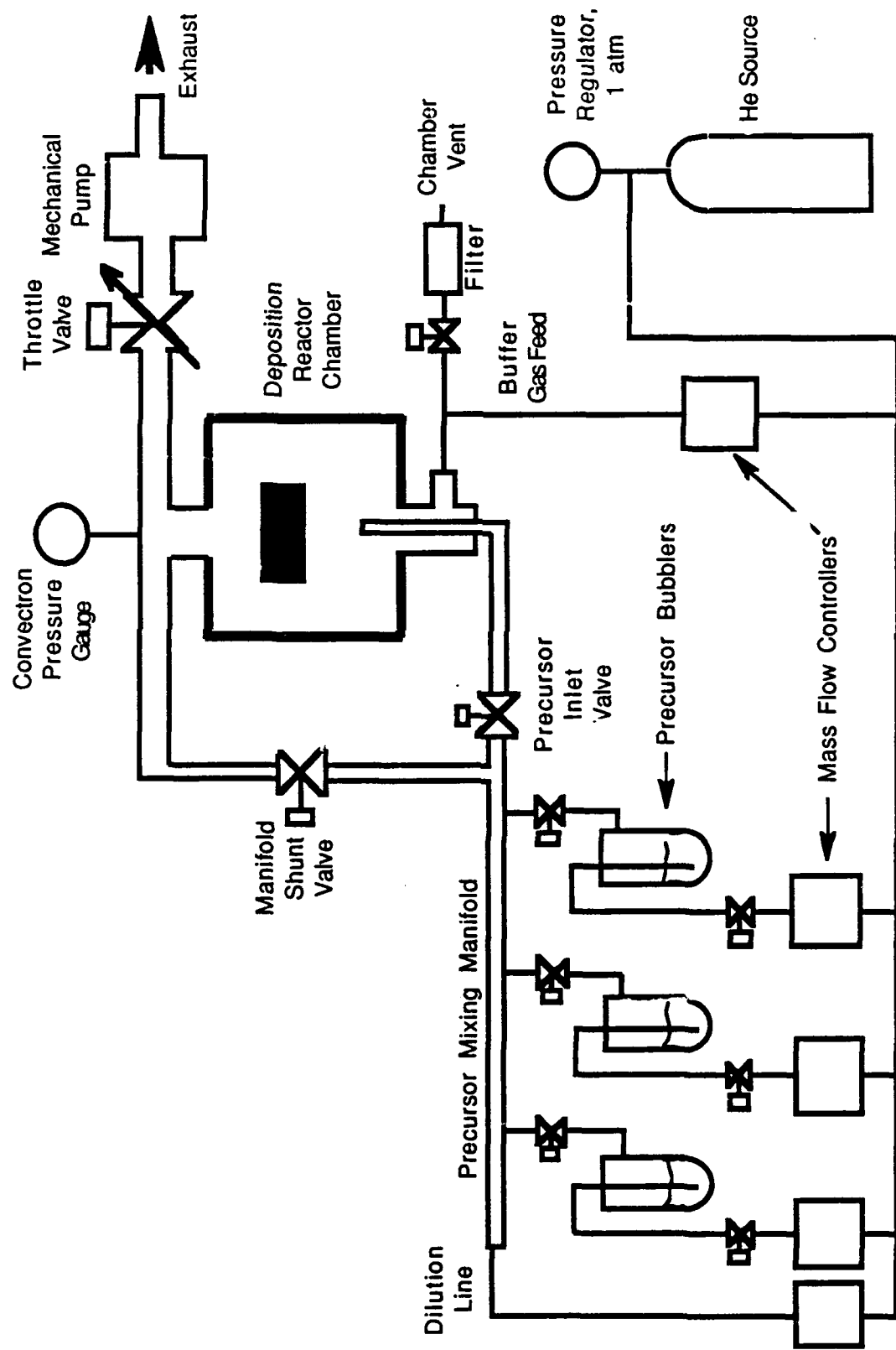


Figure 2. Test PEMOCVD System Set-up.

## Process Gases and Precursors

In these experiments, helium was used as a chemically inert medium for energy transfer from the plasma discharge to the film growth region.  $\text{He}(2^3\text{S})$ , denoted  $\text{He}^*$ , is probably the most abundant excited state species in the flowing afterglow, and exists at 19.81 eV above the ground state (9, Kolts and Setser). The afterglow may contain charged and other neutral species, however, the composition in this reactor has not yet been determined. The  $\text{He}^*$  may activate the film forming reactions by collisional energy transfer to the metalorganic precursors in the gas phase. If losses of  $\text{He}^*$  through diffusion to the chamber walls, collision with ground state helium, radiative decay, and quenching by impurities are minimized the precursor activation could be highly efficient.

Several commercially available metalorganic compounds were tried in single metal oxide depositions, those that appeared to volatilize efficiently were chosen for PZT deposition trials. The compounds used for these were tetraethyl lead, zirconium *t*-butoxide, and titanium *iso*-propoxide. At ambient temperature, tetraethyl lead and zirconium *t*-butoxide have vapor pressures of about 260 mtorr and 300 mtorr respectively. Titanium *iso*-propoxide has a vapor pressure of 1 torr at 58°C.

## Preparation and Deposition Procedures

Single oxide films were deposited on bare silicon wafers at ambient temperature. Two and three metal films were deposited on silicon wafers that had uniform electrodes consisting of a 1000 Å titanium glue layer under a 1500 Å platinum layer. These electrodes were applied by electron beam evaporation. Pre-deposition cleaning of all samples was done with a soak for several hours in an unheated 3:1 (v:v)  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$  solution, followed by a 1 - 2 minute rinse in deionized water and blow dry in  $\text{N}_2$ . After deposition, samples used for electrical tests had an array of 0.8 mm tin or gold dots evaporated on in a separate chamber, to form dot capacitors with the bottom electrode. The highest sample temperature during this step was approximately 100°C for about 20 minutes.

For PEMOCVD trials with the substrate at ambient temperature, the substrate was suspended in the reactor tube without the graphite block. For trials at elevated temperature, the graphite block with substrate attached was heated outside the chamber to the desired temperature with the quartz lamp. Thus, during deposition the external lamp only maintained the elevated temperature of the pre-heated graphite mass. The highest temperature attainable with this set-up was 350°C, therefore this was used for all the heated substrate trials.

After the heated substrate holder was placed in the quartz reactor tube the system was pumped down to approximately 50 mtorr, measured at the chamber exhaust port. With the precursor inlet to the chamber shut off, carrier flow was stabilized through the precursor bubblers with the flow diverted through the manifold shunt valve shown in Figure 2. The plasma discharge was initiated, and the precursor flow then switched from the shunt to the chamber. Chamber pressures were typically 0.3 - 0.6 torr for titanium oxide trials, 0.5 - 0.9 torr for zirconium oxide trials, and 0.9 - 1.2 torr for PZT trials. Run times were 15 to 60 minutes.

## Characterization and Results

All results presented for PZT films were obtained from samples deposited at 350°C.

SEM photos of multiple oxide films showed dense smooth film structure, as seen in Figure 3 for one PZT sample. Here the four layers - PZT, Pt electrode, Ti glue, Si substrate - are visible. The tenth-micron scale lumps are apparently part of the electrode structure. The PZT appears to have filled the electrode voids and smoothed the surface, but it has very fine scale pores or cracks. Film thickness is difficult to estimate because of the irregular film - electrode boundary, but appears to be on the order of 1000Å to 3000Å.

Energy Dispersive Spectroscopy (EDS) scans of PZT samples identified lead, zirconium, titanium, oxygen, and carbon. Unfortunately, quantitative analysis was not possible because the PZT films were too thin to mask strong interference signals from the underlying Pt, Ti, and Si substrate layers.

XRD patterns were obtained with a Scintag X-ray Diffractometer on two PZT samples, using a very shallow (86° off normal) angle of incidence. The patterns showed primarily amorphous films, but one sample did yield the weak crystalline peaks shown in Figure 4. The double peak at approximately 29° appears to coincide with perovskite PZT peaks, and the peaks at 40° and 46° are probably from the Pt electrode layer.

Electrical properties of PZT samples were measured by probing the top contacts of the dot capacitors with a Radiant Technologies RT-66A Ferroelectric Test System. This applies variable amplitude voltage pulses and measures resulting stored charge and leakage currents to generate the hysteresis loop, remanant polarization, and resistivity values. Some capacitors yielded hysteresis curves, a typical result with 2V maximum applied voltage is shown in Figure 5. Hysteresis with significant leakage current is apparent. In this test, leakage current has the effect of raising the measured polarization as the applied voltage is first lowered from its maximum. This gives the rounded shape to the loop at the maximum voltages. As explained in Figure 5, the retained charge ranged from about 0.45 to 0.75  $\mu\text{C}/\text{cm}^2$  at 2 V maximum applied voltage. Also at this voltage, the charge storage was equivalent to that obtainable from a linear dielectric material with relative dielectric constant of 200. Also, the maximum leakage currents were a few microamperes, giving resistivities on the order of 150  $\text{M}\Omega\text{-cm}$ . Leakage current became quite large at maximum voltages exceeding about 3 V, dot capacitors that were driven to electrical breakdown did so at maximum applied voltages of about 9V. Assuming a film thickness of 2000Å, this gives a breakdown field strength of 0.45MV/cm. Capacitors that gave no hysteresis were found to be highly conductive or dead shorted at the outset, before any voltages were applied.

The charge retention, fatigue, and aging behaviors of one PZT sample that had representative hysteresis response were also measured with the Ferroelectric Test System. After pulse cycling tests lasting up to 12 hours, no significant changes were found in the hysteresis behavior.

Single oxide films of titanium and zirconium were deposited on bare silicon at ambient temperature primarily to check purity and to help characterize the system parameters. A SEM photo of a titanium oxide film is shown in Figure 6. This film went down at a rate of about 30 $\mu\text{m}/\text{hr}$ , and appears to be dense and pore free. Auger analysis showed this sample to be incompletely oxidized and also found 8 - 17 at% residual carbon through the bulk of the film. Zirconium oxide samples gave similar results in X-ray Photoelectron Spectroscopy (XPS) and Auger analysis. An XPS profile of a zirconium oxide film is shown in Figure 7, this shows incomplete oxidation and significant residual carbon. High resolution scans of XPS peaks showed that this contamination was present mainly as  $\text{ZrC}_x$ , hydrocarbons, and amorphous carbon. Iron and chromium were also detected in zirconium oxide samples, particularly near the film - substrate interface.





1.5 $\mu$ m

Figure 3. SEM photo of PZT sample deposited on silicon coated with Pt:Ti electrode.

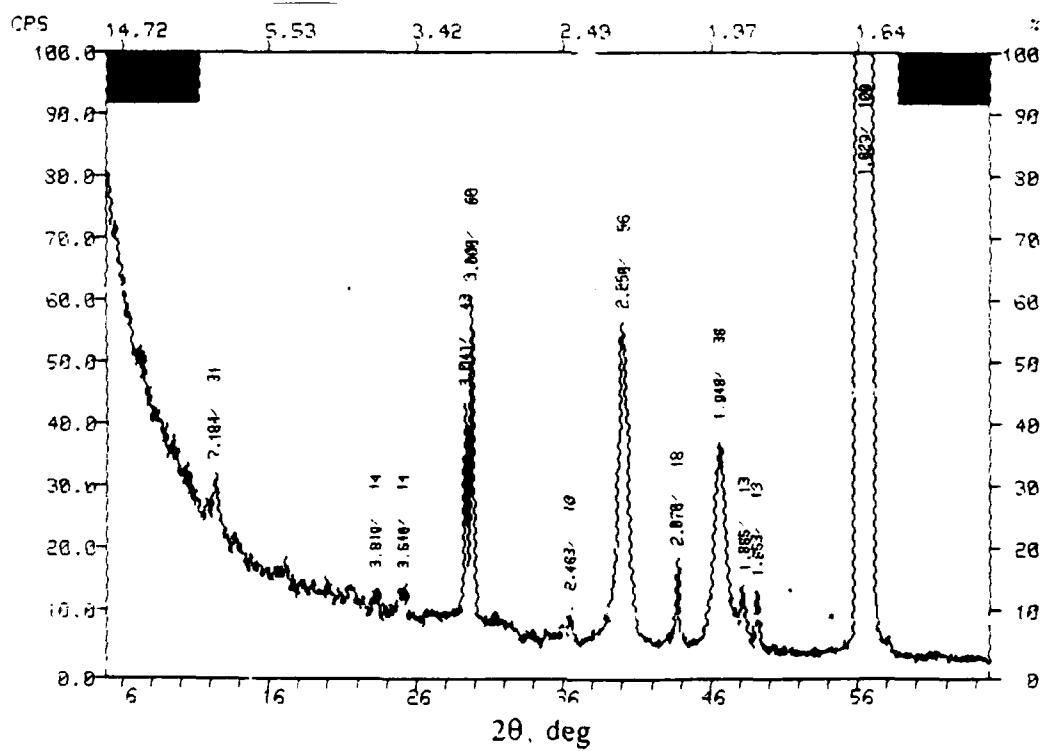


Figure 4. Shallow angle-of-incidence X-ray diffraction pattern for PZT thin film sample.

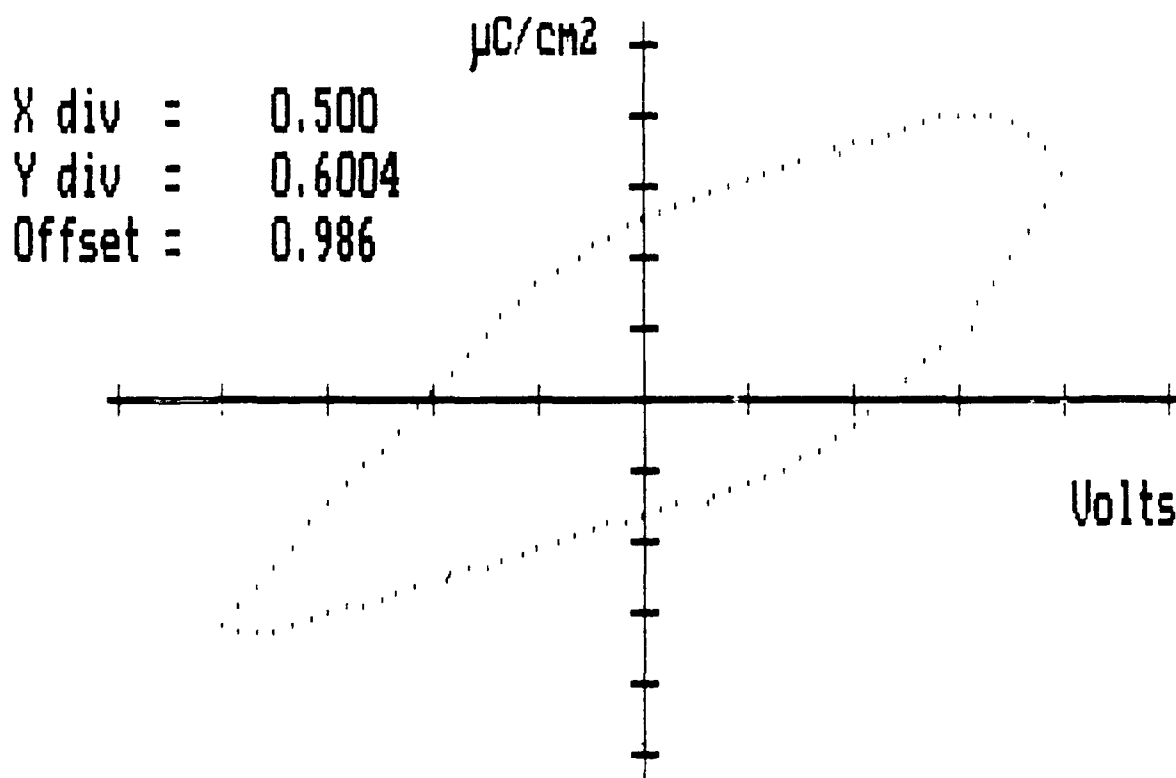


Figure 5. Ferroelectric hysteresis response for PZT thin film sample. The maximum voltage applied is 2 V. The polarization at maximum positive applied voltage (+Ps) is  $1.89 \mu\text{C}/\text{cm}^2$ . The positive and negative remanent polarizations (+Pr and -Pr) are  $1.51 \mu\text{C}/\text{cm}^2$  and  $-0.97 \mu\text{C}/\text{cm}^2$  respectively. Coercive voltages are +1.15 V and -1.04 V. Charge retention, defined as the difference between charge extracted going from -Pr to +Ps and charge extracted going from +Ps to +Pr was  $0.45 \mu\text{C}/\text{cm}^2$ . The inverse measurement, going to -Ps, gave  $0.75 \mu\text{C}/\text{cm}^2$ . Resistivities at this voltage were measured to be on the order of  $150 \text{ M}\Omega\text{-cm}$ . These values are representative of measurements made on all working capacitors on the PZT samples. Extended retention, fatigue, and aging tests conducted with maximum applied voltages of 2.25 V did not significantly change this hysteresis behavior.

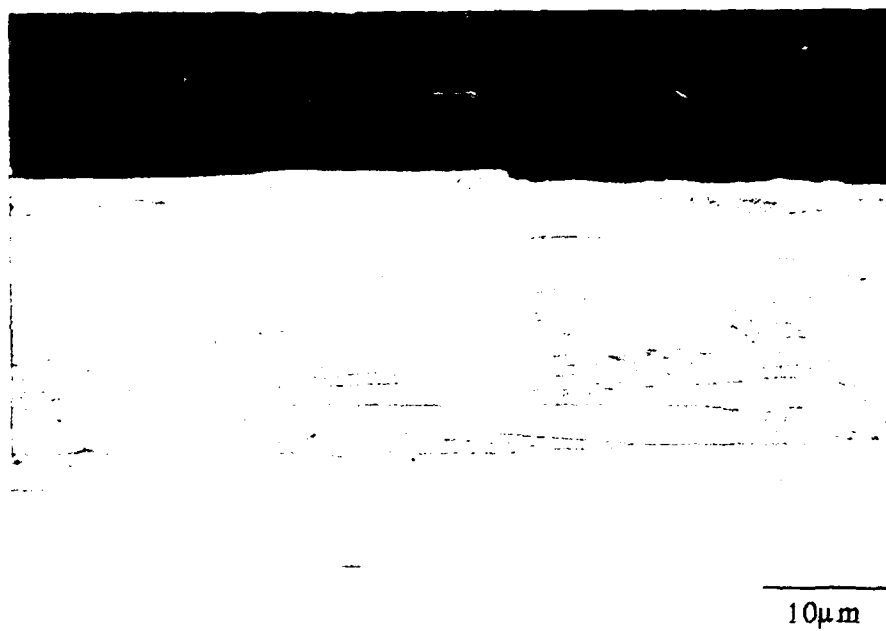


Figure 6. SEM photo of titanium oxide film deposited on bare silicon.

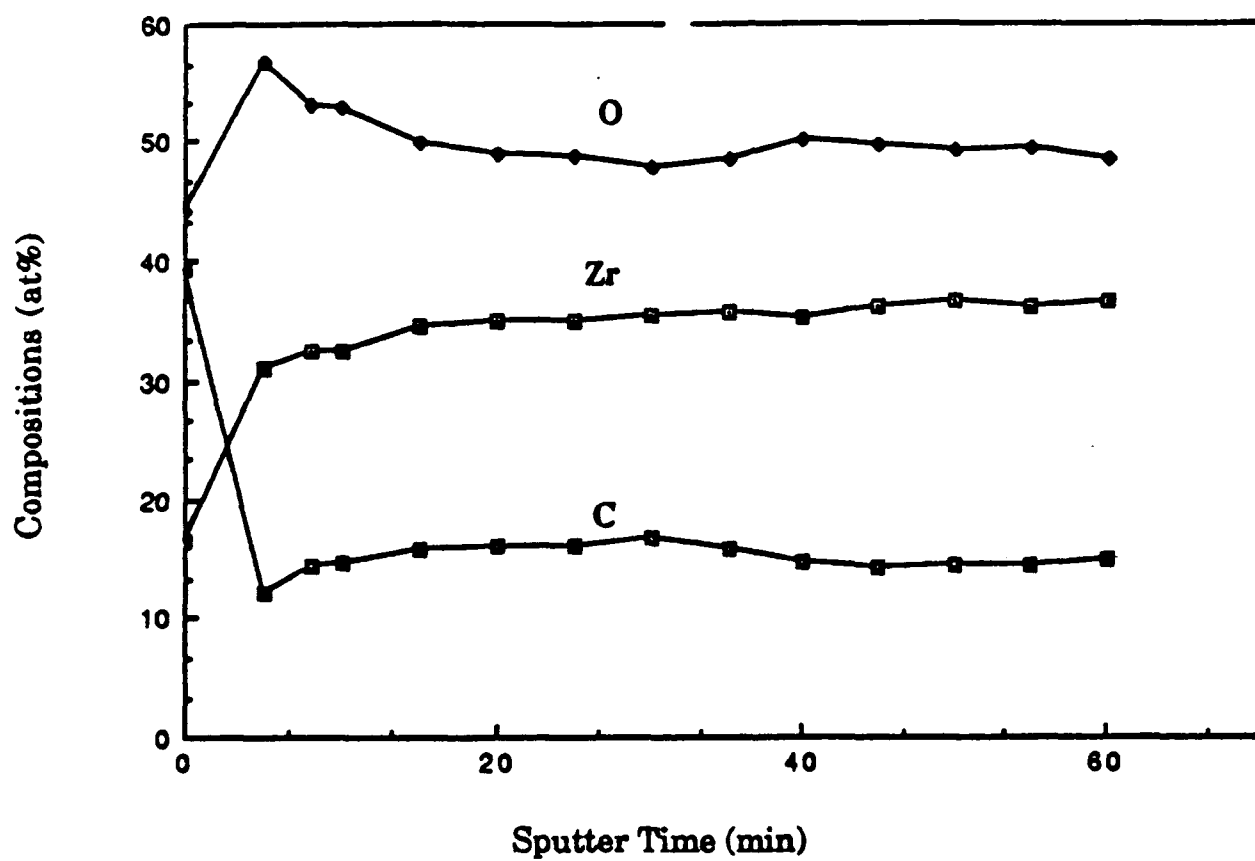


Figure 7. XPS depth profile of zirconium oxide film deposited on bare silicon.

## DISCUSSION

### Conclusions

The most significant finding is the presence of some ferroelectric hysteresis response and charge retention in PZT films grown at 350°C. Although there is clearly much work to be done to improve the material quality and electrical response of these films, the results do show promise for this deposition technique.

The electrical results show that these PZT films have much lower remanent polarization, lower breakdown field strengths, and higher leakage currents than now obtainable with sol-gel deposited films. However, the presence of any hysteresis response in these samples indicates that the electrical parameters can be improved by refining the deposition method. The retention, fatigue, and aging tests did not show significant losses in ferroelectric behavior with time or extended voltage cycling. With the low initial remanent polarization, these results are difficult to interpret. These tests will be more meaningful when higher purity and higher response samples are available.

The XRD measurements on the PZT samples show primarily amorphous structure with some evidence of perovskite crystallites. Although the results are too scant to be conclusive by themselves, they are consistent with the weak ferroelectric response. Elemental analysis by EDS could not be obtained on these films, because the films were thin and deposited on electrodes that gave strong interfering EDS signals. However, the equivalent dielectric constant of 200 is consistent with a PZT film composition rich in titanium.

The single oxide films deposited at ambient temperatures consistently showed incomplete oxidation with excess residual carbon. As noted, elemental analysis of the PZT samples is not available to directly show whether or not heating the substrate to 350°C did reduce residual carbon incorporation. It is likely, however, that the heating did reduce contamination and improve oxidation, but not enough to obtain superior electrical properties.

Iron and chromium contamination of the single oxide films may have come from problems in substrate preparation, impure precursor materials, or possibly sputtering of the RF electrodes by the plasma. It should be possible to eliminate heavy metal contamination through improved procedures, or if necessary simple modifications to the plasma generator.

### Recommendations and Plan for Future Work

These Phase I results are clearly positive enough to support further PZT film growth experiments using PEMOCVD. The first goals for future work are to improve the electrical and material properties of small PZT film samples, and to identify the deposition conditions and metalorganic precursors that consistently yield superior films at temperatures below 400°C. Once these are achieved, work towards the second goal of attaining precise control over PZT stoichiometry can begin. Finally, the next goals are to obtain uniform film thickness and composition over large areas, so that ultimately the process can be transferred to commercial production.

The immediate follow-on work must address the problems of residual carbon and incomplete oxidation, which were detected in the single oxide films. Although not directly verified, these problems are likely to also be present in the PZT samples. As the film purity and oxidation are increased, the electrical behavior should also improve. Changes in film crystallinity should also be watched for as carbon contamination is eliminated.

Several factors can be explored in the near term for their effects on film purity and composition. These include: deposition chamber pressure and gas flow rates, precursor gas phase concentration, and substrate temperature. Experiments can be done with the same precursors used for Phase I,

and can be started in the test PEMOCVD set-up with certain upgrades. These upgrades are needed to increase the reactor and pumping stack conductance and gas throughput, obtain better control of pressure and gas flow, and obtain better substrate heating over a wider temperature range. In the upgraded test PEMOCVD system, PZT and single oxide films will be deposited in greater thickness on bare silicon, glass, and electroded substrates. Thick films on bare silicon and glass will allow better analysis of composition and crystalline phase. Films on electroded substrates will undergo comprehensive electrical testing similar to that done in the Phase I effort.

If necessary in the longer term, experiments can be done to measure the effects of plasma generator design and gas additives or alternate discharge gases. In particular, ways to introduce activated oxygen to the process can be explored. These tests can be done in a new remote plasma CVD (RPCVD) reactor system which is planned to be acquired next year, or can also be done in the upgraded test PEMOCVD set-up.

Next year, alternate metalorganic precursor compounds will become available from the joint effort involving Radiant Technologies, University of New Mexico, and Sandia National Laboratories. This effort, funded by the State of New Mexico, will exclusively develop new precursors for CVD of PLZT films. However, sample compounds will be used in the PEMOCVD process development done at Radiant. Single oxide and PZT films will be generated from the precursor samples, and tested as outlined above. The films can be deposited in the purchased RPCVD reactor or in the test PEMOCVD set-up.

The purchased RPCVD reactor will be essential to the longer term development of uniform thickness and composition films over commercially practical surface areas. Acquiring this system as soon as possible will increase capability to execute the near term experiments, and will also give a head start in transferring the PEMOCVD process to ferroelectric device production.

## SUMMARY

In this Phase I study, a test set-up of a PEMOCVD reactor was used to deposit oxides of titanium, zirconium, and lead on bare silicon; and PZT on silicon coated with Pt:Ti electrodes. Tetraethyl lead, zirconium *t*-butoxide, and titanium *iso*-propoxide were used as precursors. Single oxide films were deposited at ambient temperature, PZT films were deposited at 350°C. The films were characterized by SEM, EDS, X-ray Diffraction, and XPS. In addition, PZT films were electrically characterized by a technique that uses precision charge measurements to find film polarization resulting from voltage pulses. EDS and XPS detected excessive carbon contamination and incomplete oxidation, along with trace heavy metal contamination, in the single oxide films of zirconium and titanium. The PZT samples showed ferroelectric hysteresis with retained charge of about 0.4 to 0.75  $\mu\text{C}/\text{cm}^2$ . These values did not change significantly in aging and fatigue tests. X-ray diffraction indicated presence of some perovskite crystallites in primarily amorphous PZT films. The finding of some ferroelectric behavior in films deposited at 350°C suggests that the PEMOCVD technique may be capable of growing high quality ferroelectric thin films at low temperatures that are unprecedented. Follow on experiments are planned that could improve film purity and composition, and thus result in better electrical properties and greater film crystallinity.

## REFERENCES

1. L. Parker and A. Tasch, *IEEE Circuits and Devices Magazine*, January 1990, p. 17.
2. P. Dapkus, *Ann. Rev. Mater. Sci.*, 12, 243, (1982).
3. L. Williams, P. Lu, and S. Chu, *Appl. Phys. Lett.*, 54, 1329, (1989).
4. T. Nakagawa, J. Yamaguchi, M. Okuyama, and Y. Hamakawa, *Jpn. J. Appl. Phys.*, 21, L665, (1982).
5. B.S. Kwak, E.P. Boyd, and A. Erbil, *Appl. Phys. Lett.* 53, 1702 (1988).
6. S.L. Swartz, D.A. Seifert, G.T. Noel, and T.R. Shrout, Draft Publication.
7. M. Okada, K. Tominaga, T. Araki, S. Katayama, and Y. Sakashita, *Jpn. J. Appl. Phys.*, 29, 718, (1990).
8. J. Spencer, draft submitted to *Proceedings of the 8th Symposium on Plasma Processing*, (Electrochemical Society, 1990).
9. for example; J.H. Kolts and D.W. Setser, in *Reactive Intermediates in the Gas Phase* (Academic Press, New York, 1979,) p.151.; E.E. Ferguson, F.C. Fehsenfeld, and A.L. Schmeltekopf, in *Advances in Atomic and Molecular Physics* (Academic Press, New York, 1969), vol. 5, p. 1.
10. L.G. Meiners, *J. Vac. Sci. Technol.* 21, 655, (1982).
11. P.D. Richard, R.J. Markunas, G. Lucovsky, G.G. Fountain, A.N. Mansour, and D.V. TSU, *J. Vac. Sci. Technol. A* 3, 867, (1985).
12. M.J. Helix, K.V. Vaidyanathan, B.G. Streetman, H.B. Dietrich, and P.K. Chatterjee, *Thin Solid Films*, 55, 143, (1978).
13. Y. Toyoshima, K. Kumata, U. Itoh, K. Arai, A. Matsuda, N. Washida, G. Inove, and K. Katsuumi, *Appl. Phys. Lett.*, 46, 584 (1985).
14. R.A. Rudder, G.G. Fountain, and R.S. Markunas, *J. Appl. Phys.*, 60, 3519, (1986).
15. A.D. Huelsman and R. Reif, *J. Vac. Sci. Technol. A* 7, 2554, (1989).